NAT'L INST. OF STAND & TECH R.I.C.
A11104 119770

NATIONAL INSTITUTE OF STANDARDS &
TECHNOLOGY
Research Information Center
Gaithersburg, MD 20899

ON METHODS OF OBTAINING COOLING CURVES.

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The rôle of thermal analysis in many metallurgical and chemical problems, involving in many instances the constitution and behavior of very complex substances, is of increasing importance; and great advances are being made in our knowledge of the properties of many alloys, minerals, and chemical compounds at high temperatures by means of the pyrometer.

Any internal change in the physical or chemical nature of a substance usually alters many of its physical properties, as, for example, its magnetic and thermoelectric behavior, electrical resistance, specific heat, dimensions, density, and microscopic structure. A large internal change at a definite temperature or within a small range of temperature—in other words, "a transformation"—will cause sudden or very rapid changes in some or all of these physical properties, and several of them may be used with advantage

in the detection and study of such transformations. In this paper, however, we shall confine ourselves to the consideration of such changes as may be detected, measured, and recorded by thermometric means.

METHODS OF THERMAL ANALYSIS.

All methods of thermal analysis are based upon the principle that chemical and physical transformations within a substance are, in general, accompanied by an evolution or absorption of heat. The detection of the temperature and the measurement of the extent of these transformations, and in many cases their interpretation, may be carried out by taking the cooling curve of the substance, which in its simplest form consists in plotting the temperature of the cooling substance against the time. It is evident that the heating curve of a substance may also be taken to find its characteristics, and this is sometimes done, but, in general uniform results are obtained more easily by taking the cooling curve, mainly on account of the greater experimental difficulties in maintaining a uniform rate of heating in the containing furnace. In some problems it is desirable to have both curves, while occasionally, as in transformations involving loss of water of crystallization or of constitution, the heating curves alone are of significance. The same apparatus will evidently serve for both.

The cooling curve, however exactly taken, will of course give no indication of those transformations for which there is no evolution or absorption of heat. If the cooling is at constant pressure, as we shall assume in all of what follows, the absence of a transformation—physical or chemical—may be assumed only when both the energy and the volume changes are zero. The detection of changes in volume, unaccompanied by changes in internal energy, may be effected by the use of an apparatus measuring linear expansion, such as the recording differential dilatometer of Sahmen and Tammann.[1] These cases are exceptional, however, and we shall not consider them further.

[1] *Sahmen* und *Tammann:* Über das Auffinden von Umwandlungspunkten mit einem selbst-registrierenden Dilatographen. Ann. d. Phys. **10**, p. 879–896; 1903.

There have been developed a considerable number of methods for obtaining cooling curves which are adapted to the study of recalescence points in steels as well as to the investigation of the composition and properties of alloys and chemical compounds. There has as yet been no general discussion[2] of the different methods nor of their availability for special problems and it may therefore be of some interest to have at hand an outline of the principles of the methods that may be used in obtaining cooling curves as well as a brief mention of the various types of apparatus available, with a discussion of their advantages and limitations.

The methods may be classified in various ways; thus we have to distinguish between those adapted for slow cooling, which is the case most commonly met with, and for very rapid cooling as in quenching steels; those methods which require an auxiliary body possessing no thermal transformations on cooling as compared with those requiring only the substance studied; and finally we may have on the one hand methods involving the time, and on the other hand those in which the time may be eliminated. In this paper we have considered in detail only such methods as are adapted for slow cooling, and have classified them in terms of the forms of the curves representing the experimental data.

Many operations which can be carried out in the laboratory can not be applied conveniently in industrial works, so that it will be necessary also to distinguish the various types of apparatus as regards their adaptability either for purely scientific researches or for industrial needs. For the latter, especially, it is very desirable to make all operations as automatic as possible, so that the different methods of autographic and photographic recording should be considered. Again, we shall have occasion to point out those methods which are the most advantageous to use when very minute quantities of heat or differences in temperature are to be detected, as, for example, the secondary breaks in the cooling

[2] A paper by *W. Rosenhain*, on "Observations on Recalescence Curves" was read before the London Physical Society, January 24, 1908, an abstract of which indicates he has compared the merits of the "Inverse Rate" and "Differential Methods."

The Differential Method has also been studied in detail by *Portevin*, Notes sur l'Emploi du Galvanomètre Différentiel, Rev. de Métallurgie, **5**, p. 295; 1908.

curves of many alloys and of numerous compounds and mixtures. In such cases it becomes necessary to use methods of the highest possible sensitiveness, which usually necessitates the discarding of autographic and photographic recording.

We shall mention those methods which are suitable for taking cooling curves in the range of temperatures up to 1500° C, but much of what is said will apply also to higher temperatures if proper precautions be taken to eliminate the effects upon the measuring apparatus of the electrical conductivity of the materials and contents of the furnace. Although several methods of measuring temperature may be used over most of the range indicated, such as the change of electrical resistance of platinum with temperature and the various optical and radiation pyrometers, we shall confine ourselves to the thermoelectric pyrometer made of the platinum metals as being on the whole the most generally suitable over this range for this kind of work, although undoubtedly particular problems may occur in which the use of some other type of pyrometer is preferable.

Use of the Thermocouple.—It may be recalled that the thermocouple possesses most of the desirable attributes of a temperature indicator. With its insignificant volume it may be introduced into a very small space, and so be used with small samples, and it takes up the temperature of the sample with great promptness. When made of the platinum metals, it is very durable and retains the constancy of its indications in a most satisfactory way, even when subjected to contaminating atmospheres, and after deterioration it may usually be restored to its former condition by glowing. Temperatures may be obtained by means of a simple form of galvanometer without any accessories. Such a galvanometer, it is true, indicates electromotive forces, while in general the temperature of a thermojunction is not strictly proportional to the electromotive force generated by it, although such a linear relation, which it is desirable to realize in order to simplify the interpretation of the indications of some types of recording instruments, holds very nearly in the case of the platinum-iridium couple of the composition Pt, 90 Pt—10 Ir.

The following table shows the E.M.F.—Temperature relation, and the E.M.F. in microvolts per degree centigrade (dE/dT) for

couples composed of a wire of pure platinum joined to one of the approximate composition: *90 Pt—10 Rh*, *90 Pt—10 Ir*, and pure *Ni*, respectively.

Temp. Cent.	Pt, 90 Pt—10 Rh		Pt, 90 Pt—10 Ir		Pt, Ni	
	E.M.F. Microvolts	dE/dT	E.M.F. Microvolts	dE/dT	E.M.F. Microvolts	dE/dT
300	2290	9.0	4080	15.9	7940	11.8
500	4160	9.7	7300	16.7	10510	14.4
700	6170	10.4_5	10720	17.5	13670	17.1
900	8340	11.2	14300	18.3	17400	19.7
1100	10630	11.9	18030	19.1	21640	22.4
1300	13070	12.6	21940	19.9	26300	25.0
1500	15600	13.3_5	26010	20.7	.....	.....

It will be seen that the platinum-iridium couple is nearly twice as sensitive as the platinum-rhodium couple beside having a more nearly linear E.M.F.—Temperature curve. These advantages are in part offset, however, by the fact that the iridium couple deteriorates more rapidly and is less constant in its indications. The platinum-nickel couple, although very sensitive, is less reliable than the others and the *Ni* wire soon becomes brittle and breaks. Moreover, the effect of the nickel recalescence point (about 375° C) has some influence on readings taken in its neighborhood. There are other thermojunctions, made of alloys of the more refractory baser metals, which are much more sensitive than the above and which may be suitable over particular ranges. These couples are usually constructed of wire of considerable diameter and are, therefore, not adapted for work with small samples. For exact work one should make sure of their constancy of indication over the temperature range to be studied. A more robust and less sensitive indicating instrument may evidently be used with this type of thermocouple, although recently pivot instruments, suitable for use with the platinum couples, have been constructed by Paul of London, the Cambridge Scientific Instrument Company, and by Siemens and Halske.

Methods of Recording.—Before describing the various methods that have been suggested for the taking of cooling curves, it may be well to consider the ways in which the observations may be recorded. Either the observer may himself read and record the indications of the instruments and discuss the data so obtained, analytically or graphically; or he may use, if the method and desired precision permit, an autographic or a photographic self-registering instrument, when it may or may not be necessary to make further reductions, depending upon the method used and the interpretation sought.

It is evidently of great advantage to use self-recording apparatus when possible, and it then becomes necessary to choose between the photographic type and the autographic.[3] The latter possesses the advantage that the experimenter may watch any part of the record, and can therefore control the operation and at any moment vary the conditions affecting the experiment; whereas with a photographic recording apparatus, as usually constructed, the observer does not know whether or not the experiment is progressing properly until it is finished and he has developed the sensitive plate. The manipulation by the photographic method is usually also more delicate and time consuming and the adjustment less sure, and the record often requires further graphical interpretation. The autographic method is in general not adapted for interpreting phenomena taking place within an interval of a few seconds, so that for very rapid cooling it is necessary to employ the photographic method. It is possible to construct the photographic recorder so as to obtain a very considerable range of speeds with the same apparatus, while it is difficult and costly to construct an autographic recorder having more than two speeds.

TEMPERATURE—TIME CURVES.

I. θ *vs* t.—The simplest method of obtaining a cooling curve is to take simultaneous measurements of the temperature of the cooling substance and of the time, from which a plot may be made showing the variation of temperature with time. (See Plate I, Fig. I.)

[3] The term *autographic* is here used to designate an instrument which is self-recording by any other than photographic means.

The most obvious defect of this method is that it will not distinguish between phenomena proper to the substance studied and those due to outside conditions, such as accidental variations in the rate of cooling of the furnace due to air drafts and like causes. Again, where measurements over a considerable range of temperature are to be taken continuously, it becomes impracticable without elaborate experimental arrangements to combine great sensibility with this great range, so that the experimenter is in general forced to choose between great sensibility over a small temperature range or a relatively small sensibility over a large range; and this is especially true if it is desired to record the data automatically.

This method was naturally the first used[4] and it is to-day perhaps the most common one for taking cooling curves in both metallurgical and chemical laboratories. In its most elementary form it requires a minimum of apparatus—a thermocouple and an indicating galvanometer. Any desired sensibility and range may be had by substituting for the direct reading galvanometer a potentiometer and sensitive galvanometer. With this arrangement it is advantageous, when rapidity of observation is an object, to measure the last increment of temperature in terms of the galvanometer deflection rather than try to balance the potentiometer exactly while the temperature is changing. It is possible in this way to take readings as often as every 5 seconds with a properly devised set-up and quick period galvanometer.[5] A precision of 0°.1 C at 1000° C may be attained. Independently of the method of measurement used, the certainty of the detection of slight transformations may usually be increased by increasing the size of the sample under observation, thus making available larger quantities of heat.

The constant attention of the observer is of course required for either of the above systems of measurement. There have been devised, however, many kinds of self-recording apparatus for using this method, the earlier forms being photographic, while many of the later ones are autographic.

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[4] Frankenheim, Pogg. Ann. der Physik. **37**, **38** (1836–1837).

[5] See W. P. White, Potentiometer Installation, Phys. Rev. **25**, 334; 1907.

Photographic Recorders.—Among the earliest photographic recorders we may mention the apparatus of Roberts-Austen [6] (Fig. 1) in which the photographic plate P was given a vertical motion, either by clockwork, or, in order to secure maximum sensibility for several rates of cooling, by means of buoying the plate on water whose rate of flow could be regulated. The vertical motion of the plate then gave the time while the deflection of the

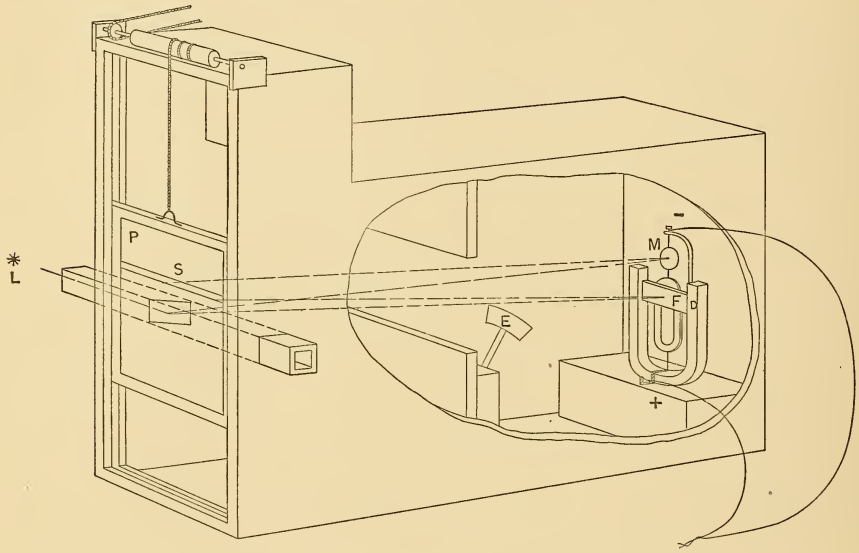

Fig. 1.

galvanometer gave the corresponding temperature, and a beam of light from the source L, reflected from the galvanometer mirror M and incident on the plate, after passing through a fine slit *S* placed horizontally before the moving plate, gave directly on the latter the time-temperature curve. Light reflected from a fixed mirror F and interrupted at equal intervals by a pendulum E gave a fixed zero line as well as a measure of the regularity of the motion of the plate. It was the practice later,[7] when taking measure-

[6] Proc Royal Society, **49**, p. 347; 1891. Nature, **45**, p. 534; 1892. First Report of the Alloys Research Committee in Proc. Inst. Mech. Engs. 1891.

[7] Fourth Report of the Alloys Research Committee, Proc. Inst. Mech. Engs., 1897. A. Stansfield, Phil. Mag. **46**, p 59; 1898.

ments over short temperature ranges, to increase the sensibility by balancing the greater part of the E.M.F. of the thermocouple with an auxiliary measured E.M.F., and giving the galvanometer the maximum sensibility that would keep its deflections on the plate.

In the apparatus used by Charpy,[8] or in its very elaborate form as constructed by Toepfer, of Potsdam, for Kurnakow,[9] the vertically moving plate is replaced by a rotating cylinder wound with the sensitized paper on which the deflections of the galvanometer are registered. This form of recorder had also been used and discarded by Roberts-Austen. Kurnakow's apparatus, which must be placed in a dark room, is furnished with an auxiliary telescope and scale system using red light, so that the experiment may be controlled during the taking of a record. As constructed, five speeds may be given to the cylinder; and there is provided an E.M.F. compensating system for maintaining the maximum sensibility over a series of temperature ranges.

There is another device, used by C. L. A. Schmidt,[10] by which the experiment may be watched while a photographic record of a cooling curve is being taken. It consists in shunting the sensitive photo-recording galvanometer G (Fig. 2), in series with a high resistance R, across a direct reading millivoltmeter V. If the resistance of R+G is great compared with that of V, the readings

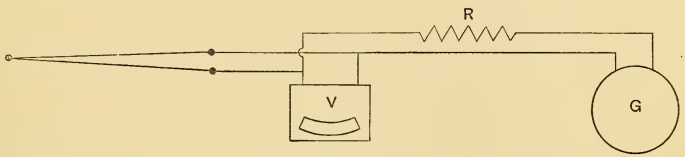

Fig. 2.

of the millivoltmeter will not be altered appreciably by this operation. Schmidt moves the photographic plate, mounted as in the apparatus of Roberts-Austen, by means of a screw driven by a small motor. In this way any desired speed may be given to the plate.

[8] G. Charpy, Bull. de la Soc. pour l'Encouragement, **10**, p. 666; 1895.
[9] N. S. Kurnakow, Zs. f. Anorg. Chemie, **42**, p. 184; 1904.
[10] C. L. A. Schmidt, Chem. Eng., **6**, p. 80; 1907.

In practice it has been found difficult to realize conveniently a sufficiently steady motion of the plate in the Roberts-Austen system of recording, and attempts have been made to devise methods in which the photographic plate remains fixed in position. This has been successfully accomplished by Saladin, whose apparatus (Fig. 8, p. 215) has been modified by Wologdine[11] to give the temperature-time curve by removing the prism M and substituting for the second galvanometer G_2 a plane mirror turning about an horizontal axis. This mirror may be controlled by an hydraulic system as in Roberts-Austen's apparatus, or by clockwork as in the model constructed by Pellin, of Paris. The deflection of the galvanometer G_1 gives to the beam of light an horizontal motion over the plate proportional to the temperature, while the vertical motion of the beam of light is given by the mirror turning at a uniform rate, and is therefore approximately proportional to the time as registered on a flat plate.

Autographic Recorders.—To obtain a satisfactory autographic or pen record without sacrifice of sensibility of the galvanometer it is necessary to eliminate the friction of the pen or stylus upon the paper. This has been accomplished by the use of mechanisms which cause the pen or stylus at the end of the galvanometer boom to make only momentary contact with the moving paper.[12]

In the Siemens and Halske[13] form of instrument, Fig. 3, the paper P is driven forward by the same clockwork that controls the pressing down, by means of the arm B, of the stylus N, which imprints dots periodically on the paper by means of a typewriter ribbon running across and beneath the record sheet. This system permits of taking a record continuously over very long periods of time. In most of the other recorders the paper is wound upon a

[11] S. Wologdine, Rev. de Métallurgie, **4**, p. 552; 1907.

[12] There are a considerable number of thermoelectric recorders. Among the manufacturers of these instruments are: Siemens and Halske, Berlin; Hartmann and Braun Frankfort a. M ; Pellin, Chauvin and Arnoux, Carpentier, and Richard, Paris; Leeds and Northrup, and Queen, of Philadelphia; The Scientific Instrument Company, of Cambridge, England and Rochester, N. Y.; The Bristol Company, Waterbury, Conn.

[13] Zs. f. Instrk., **24**, p. 350; 1904.

drum, and various devices are used to obtain the record; thus in the Hartmann and Braun type a silver stylus makes sulphide dots on a prepared paper, and in the Cambridge thread recorder rectangular coordinates are obtained by having the galvanometer boom strike an inked thread which runs parallel to the drum.

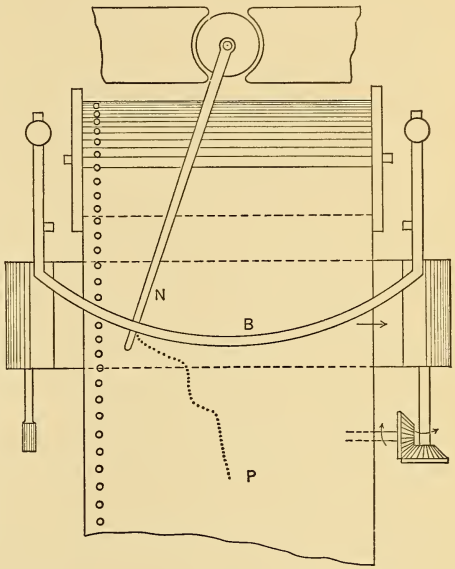

Fig. 3.

As previously stated, these autographic instruments all give intermittent records and are limited to one or two speeds, and although they may be made very sensitive they are not adapted for the detection of transformations which take place very rapidly, since the recording interval can not readily be shortened much below 10 seconds, and in most instruments this interval is greater than 15 seconds. In other words, they can be used advantageously only for slow cooling.

II. θ *vs* t, θ *vs* t' (*or* θ *vs* θ').—In order to eliminate the effect of irregularity of outside conditions which influence the rate of cooling, a method commonly used when endeavoring to detect small transformations consists in placing a second thermocouple in the furnace, but sufficiently removed from the substance studied to be uninfluenced by its behavior. Alternate readings on the temperature of the test piece (θ) and of the furnace (θ') are then taken, preferably at definite time intervals. The data are most readily discussed by plotting the two temperature-time curves side by side as shown in Fig. 4, or by plotting the difference in temperature θ–θ' against the temperature θ of the test piece.

This method may be made recording either by using two instruments or by modifying one of the above mentioned autographic recorders so as to trace the curves of two thermocouples on the same sheet.[14] In practice, however, this method is usually resorted to only when great sensibility is desired, as in detecting minute internal energy changes, when the potentiometer combined with the deflection galvanometer is the most sensitive and quick-working arrangement for taking the measurements. (See p. 205.) It is convenient to use thermocouples of the same composition so as to have readings of both the temperature of the sample and of the furnace given by the same potentiometer setting, and so depend upon the galvanometer deflections for measuring the residual parts of θ and θ'.

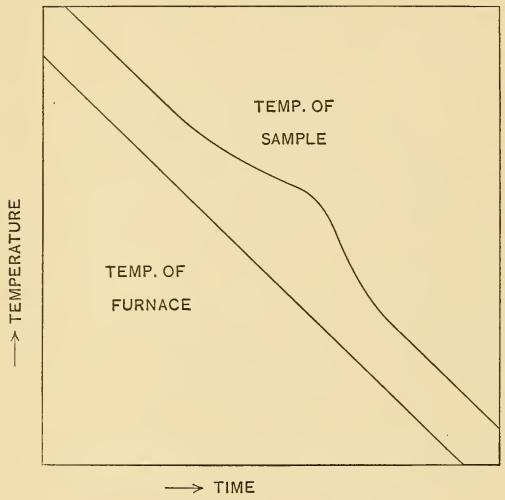

Fig. 4.

Regarding the precision of this method, it is to be noted that the quantity it is really desired to measure is $\theta-\theta'$ in terms of θ, and this is accomplished by measuring θ and θ', hence the sensibility of $\theta-\theta'$ is no greater than that of θ or θ'. In other words the method requires the maximum refinement of measurement to obtain the quantity sought, as well as the maximum of computation or plotting to reduce the observations.

DIFFERENTIAL CURVES.

III. *θ vs t, $\theta-\theta'$ vs t.*—The preceding method, II, may readily be modified so as to give $\theta-\theta'$, the difference in temperature between the test piece and furnace, by direct measurement instead of by computation, with the added advantage that the

[14] The Siemens and Halske instrument has been so arranged. See Zs. f. Instrk., 24, p. 350; 1904.

precision of $\theta-\theta'$ may be made very great as compared with that of θ, the temperature of the sample. This may be accomplished, for example, by placing a commutator in the thermocouple circuit at A, Fig. 5, so that alternate measurements on θ and $\theta-\theta'$ may be taken in terms of the time. Evidently the connections may be so made that either the galvanometer G_2 of the same direct reading or potentiometer system that measures θ, or a separate instrument G_1, as shown in the figure, may be used to measure $\theta-\theta'$.

Use of a Neutral Body.—Accidental variations in the indications of the auxiliary thermocouple giving θ', the furnace temperature may largely be eliminated by placing this couple within a blank or neutral substance. The material of the neutral body should be such that it undergoes no transformations involving an absorption or evolution of heat within the temperature range

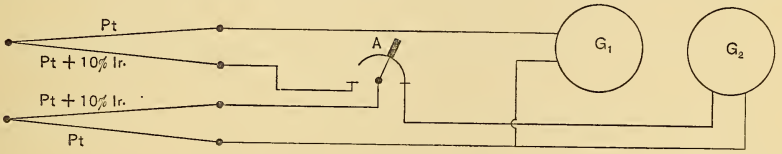

Fig. 5.

studied, such as a piece of platinum, porcelain, or even in some cases nickel or nickel steel. It is also desirable that the sample and neutral have as near as may be the same heat capacities and emisivities. The sample to be studied and the neutral piece are placed near together and arranged symmetrically with respect to the temperature distribution within the furnace.

To Roberts-Austen [15] again was due the credit of first devising a sensitive differential method using the neutral body. He also modified his photographic recorder (Fig. 1) so as to give, by means of a second galvanometer, the $\theta-\theta'$ *vs* t curve on the same plate with the θ *vs* t curve, from which a curve giving $\theta-\theta'$ in terms of θ could be constructed. His arrangement of the direct reading and differential thermocouple and galvanometer circuits

[15] Fifth Report of the Alloys Research Committee, Proc. Inst. Mech. Engs., p. 35; 1899. Metallographist, 2, p. 186; 1899.

is shown in Fig. 6 in which S is the sample or test piece and N the neutral body possessing no transformations; the galvanometer G_2 measures the temperature θ of the sample, and G_1 measures the difference in temperature $\theta-\theta'$ between the sample and the neutral. Curves for steels and alloys were usually taken with the samples in vacuo.

It is evident that Roberts-Austen's final photographic apparatus, although very sensitive, was also complicated and very delicate of adjustment, and in practice it took great skill in its use, requiring for instance some three or four successive exposures adjusted to the proper adjacent temperature ranges, to take the cooling curve of a steel from 1100° C to 200° C.

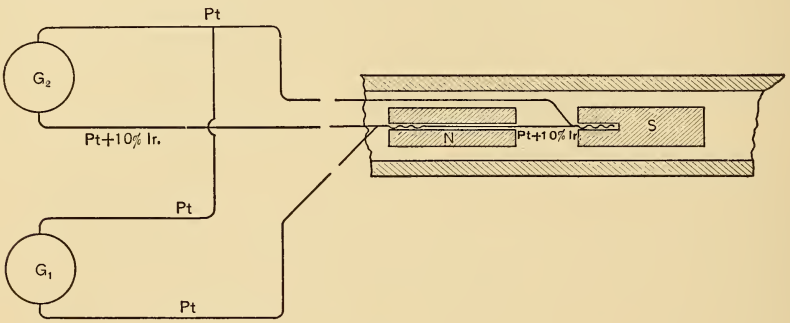

Fig. 6.

Most of the recent exact work [16] employing the principle of this method has been done by taking the observations of θ directly on a potentiometer and $\theta-\theta'$ on the same or an auxiliary galvanometer. In this case of direct reading, the simpler arrangement of thermocouples indicated in Fig. 5 may advantageously replace Roberts-Austen's (Fig. 6), or the modification shown in Fig. 7, such as used by Carpenter and others, thus dispensing with one thermocouple and the drilling of a second hole in the sample.

This method is evidently capable of attaining maximum sensitiveness since the galvanometer connected to the differential thermocouple, giving $\theta-\theta'$ *vs* t, may be made as sensitive as desired independently of the θ *vs* t system. There is the further

[16] See for example: Carpenter and Keeling, Collected Researches, Natl. Phys. Lab., **2**, 1907.

advantage that no limits are set to the range of temperatures over which a given precision in $\theta-\theta'$ may be had. There is, however, a limitation on the certainty of interpretation of results by this method, especially when the rate of cooling is rapid, due to the fact that it is practically impossible to realize the ideal condition of having $\theta-\theta' =$ a constant, or keeping the cooling curves of the test piece and neutral parallel for temperature intervals within which there are no transformations of the test piece. The rate of cooling, and hence the value of $\theta-\theta'$, is influenced by several factors, among the most important of which are the mass of each substance—the unknown and the neutral—its specific heat, conductivity, and emissivity, as well as the relative heat capacities of the furnace and inclosed samples. The $\theta-\theta'$ *vs* t line is, however, always a smooth curve, except for the regions in which there are transformations in the substance under study.

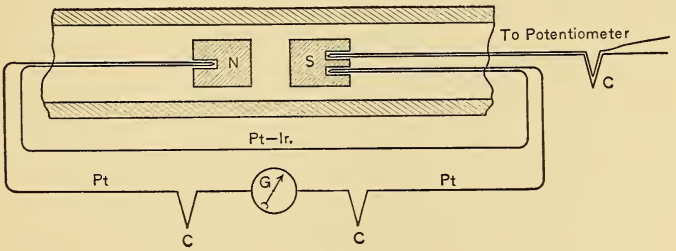

Fig. 7.

The autographic system of recording may also be used, and it is possible to construct an apparatus by means of which both the θ *vs* t and $\theta-\theta'$ *vs* t curves shall be recorded simultaneously on the same sheet by the same galvanometer boom. In order to accomplish this we have made use of a Siemens and Halske recording millivoltmeter having a total range of 1.5 millivolts and a resistance of 10.6 ohms. The E.M.F. generated by the differential thermocouple, proportional to $\theta-\theta'$, is recorded directly by this instrument. 1° C corresponds to from 16 to 19 microvolts between 300° and 1100° C for a platinum-iridum couple, or to about 1.8 mm on the record paper. In series with the Pt-Ir thermocouple giving temperatures is a suitable resistance, about 200 ohms in this case, so that the galvanometer boom may be kept

within the limits of the paper when recording values of θ. The circuit is made alternately through the direct and the differential thermocouple circuits in series with the recorder by means of a polarized relay actuated by the same battery that depresses the galvanometer boom when the mark is made on the paper. The thermocouple circuits may be those of either Figs. 5, 6, or 7, but with the galvanometer G_2 indicating temperatures suppressed. It is evident that by recording the two curves, $\theta-\theta'$ *vs* t and θ *vs* t, on the same sheet there is some sacrifice in the ability to detect small and rapid transformations, since the spacing is doubled. Usually also, with such an arrangement, the galvanometer will not be completely aperiodic for one or the other system. On the other hand, it is of great advantage to have the curves together and obtained independently of inequalities in clock rates, which are a serious source of error in locating transformation points exactly when two separate instruments are used.

When it is desired merely to detect the existence of a transformation without measuring its temperature exactly, the sensitive form of recording millivoltmeter may be connected directly to the differential thermocouple without other accessories.[17]

IV. θ *vs* $\theta-\theta'$.—It is sometimes of advantage to be able to record and discuss the data independently of the time, and so express $\theta-\theta'$, the difference in temperature between sample and neutral, directly in terms of θ, the temperature of the sample. This may evidently be accomplished by replotting the results obtained from the curves of the previous differential methods which involve the time. It was reserved, however, to Saladin, engineer of the Creusot Works, to invent, in 1903, a method [18] that would record photographically the θ *vs* $\theta-\theta'$ curve directly, thus obviating any replotting. His method possesses also the advantage of having the photographic plate fixed in place. The forms of curve obtained in this way are illustrated in Plate I, Fig. IV.

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[17] Hoffmann und Rothe, Zs. Instrk., **25**, p. 273; 1905.

[18] Saladin: New Autographic Method to Ascertain the Critical Points of Steel and Steel Alloys, Iron and Steel Metallurgy and Metallography, **7**, p. 237; 1904. First presented at Reunion des Membres français et belges de l'association Internationale des Methodes d'Essais, 28 Fev., 1903.

The arrangement of the apparatus in its simplest form, due to Le Chatelier,[19] is shown in Fig. 8. Light from the source S strikes the mirror of the sensitive galvanometer G_1 whose deflections measure the differences in temperature $(\theta-\theta')$ between the sample under study and the neutral body. The horizontal deflections of the beam of light are now turned into a vertical plane by passing through the totally reflecting prism M placed at an angle of 45°. A second galvanometer G_2, whose deflections are a measure of the temperature of the sample and whose mirror in its zero position is at right angles to that of G_1, reflects the beam horizontally upon the plate at P. The spot of light has thus

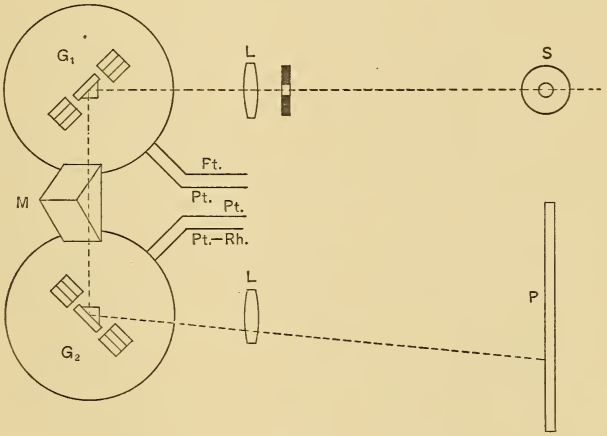


Fig. 8.

impressed upon it two motions at right angles to each other, giving, therefore, on the plate a curve whose abscissæ are approximately proportional to the temperature θ of the sample and whose ordinates are proportional to $\theta-\theta'$. The sensitiveness of the method depends upon that of the galvanometer G_1, which may readily be made to give five or six millimeters for each degree centigrade. The arrangement of the thermocouple circuits is the same as in Figs. 6 or 7. If so desired, the time may also be recorded by means of a toothed wheel driven by a clock and placed in the path of the beam of light. Compact forms of

[19] H. Le Chatelier, Rev. de Métallurgie, **1**, p. 134; 1904.

this apparatus, which is used considerably in metallurgical laboratories, are made by Pellin, Paris, and by Siemens and Halske, Berlin.

When steels and metallic alloys in the solid state are being investigated, advantage may be taken of the thermoelectric behavior of the sample itself to record the critical regions with Saladin's apparatus. Thus Boudouard[20] measures $\theta-\theta'$ by means of platinum wires set into crevices at each end of the sample, taking advantage of the fact that the transformation will usually be progressive along the sample. This modification eliminates the neutral piece and one platinum or alloy wire, but, as Le Chatelier has shown,[21] is less accurate than the usual form of Saladin's apparatus; and its indications may even be indeterminate or ambiguous, as the reaction may start midway between the embedded wires or at either end.

Saladin's method, it should be noted, is a perfectly general one for recording the relations between any two phenomena which may be measured in terms of E.M.F. or as the deflections of two galvanometers. This method can not readily be made autographic, as this would require the simultaneous action of two galvanometer systems on a single pen. When used as a direct reading method it reduces to III.

IVa. θ *vs* $\theta-\theta'/\Delta\theta$.—For even moderately rapid cooling the differential method gives distorted curves which are often difficult of interpretation. This distortion is due largely to the different heat capacities and emissivities of the sample and neutral piece, thus causing differences in their rates of cooling in the furnace. Rosenhain has suggested (l. c.) that these irregularities may be eliminated by taking what he calls the "Derived Differential Curve," or expressing the temperature θ of the sample in terms of the difference in temperature $\theta-\theta'$ between the sample and neutral for equal temperature decrements $\Delta\theta$ in the sample. The experimental method is the same as in IV, but in addition it is necessary to replot the data obtained from the θ *vs* $\theta-\theta'$ measurements so as to give the value of $\theta-\theta'$ per degree change

[20] O. Boudouard, Rev. d. Metallurgie, **1**, p. 80; 1904.
[21] Rev. de Metallurgie, **1**, p. 134; 1904

in temperature of the sample in terms of its temperature; but this appears to be worth while when the cooling curves of the sample and of the neutral differ considerably.

DIRECT AND INVERSE RATE CURVES.

V. θ *vs* $d\theta/dt$.—In many problems it is of interest to measure the speed of the transformations under observation. This may be done by determining directly the rate of change of temperature of the sample in terms of its temperature. Le Chatelier [22] used this method in 1887 in his study of the properties of clays. He was also the first to employ a photographic apparatus for the recording of cooling or heating curve data, using an arrangement in which the plate remained stationary. The sparks from an induction coil were made to pass at intervals of two seconds before a slit and gave upon the plate, after reflection from the galvanometer mirror, images of the slit whose spacing was a measure of the speed of heating, which in his experiments was about 2° C per second.

Another method of recording the rate of heating or cooling in terms of the temperature has been devised by Dejean.[23] The new feature of this method is the use of an induction galvanometer or relay which may be inserted in the circuit of the more sensitive galvanometer G_1 of the Saladin system (Fig. 8). The principle of the apparatus is shown in Fig. 9. The induction

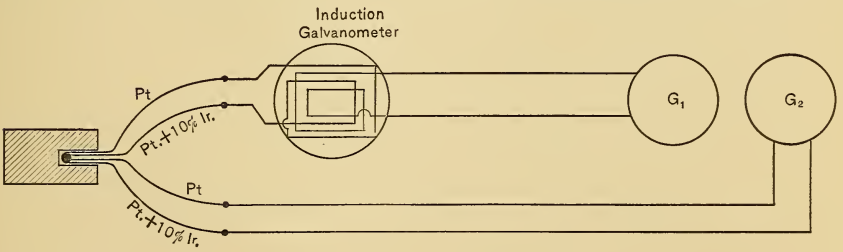


Fig. 9.

relay is a modified d'Arsonval galvanometer having an electromagnet and a movable coil, the latter consisting of two distinct

[22] H. Le Chatelier, Comptes Rendus (Paris), **104**, p. 1443; 1887.
[23] P. Dejean, Rev. de Metallurgie, **2**, p. 701; 1905. **3**, p. 149; 1906.

insulated windings, one of which is connected to a thermocouple. Heating or cooling one junction of this couple causes the coil to be deflected and its motion in the field of the electromagnet induces an E. M. F. in the second winding of the coil which is proportional to its angular speed and hence to the rate of change of E. M. F. of the couple, or approximately to the rate of cooling or heating, i. e., to $d\theta/dt$. The induced E. M. F. is measured by joining this winding to the sensitive galvanometer G_1. The galvanometer deflection passes through a minimum when the heating or cooling passes through a minimum, that is for a region in which there is an absorption or evolution of heat. A second thermocouple in series with the other galvanometer G_2 of the Saladin system gives the temperature of the sample. We have, therefore, on the plate P (Fig. 8) when the record is taken photographically, the temperatures as abscissæ and the rate of cooling $d\theta/dt$ as ordinates as shown in Plate I, Fig. V. Dejean has used this method in the study of steels and has also investigated with it the copper-cuprous oxide system. The transition temperatures are very sharply marked. If desired, direct reading may be substituted for the photographic recording, with an increase in precision, as discussed on p. 205. This method is evidently a perfectly general one for recording the rate of change of E.M.F. (dE/dt).

For neither Le Chatelier's nor Dejean's arrangement can differences in the rate of heating or cooling due to the substance itself be distinguished from those due to external causes, since no neutral piece is used.

VI. θ *vs* $dt/d\theta$.—Among the methods adapted for slow cooling, we shall mention last one of the earliest which was used to throw into prominence the abnormalities of a cooling curve, namely, the *inverse rate method*, which was employed as early as 1886 by Osmond[24] in his classic researches in metallurgy. It consists in noting the intervals of time required for a substance to cool by equal decrements of temperature and plotting this quantity ($dt/d\theta$) in terms of the temperature. (See Plate I, Fig. VI.) Osmond thus describes his method: "The time taken by the ther-

[24] F. Osmond, Comptes Rendus (Paris), **103**, p 743, p. 1122; 1886. **104**, p. 985; 1887. Annales des Mines, **14**, p. 1; July, 1888.

mometer during the heating or cooling of the sample to rise or fall one division of the scale (1 mm) was registered by means of a Morse telegraph ribbon or on a rotating cylinder turned by a small electric motor. * * * A halt of the thermometer is transcribed as a cusp and a slowing down by a swell of the curve, whose area is proportional to the quantity of heat set free "

But one thermocouple is needed and no neutral piece is used, so that the apparatus is the same as required for a θ *vs* t curve, I, although it is necessary, if work of precision is to be undertaken, to record very exactly by means of a chronograph and key the intervals of time (Δt) required to pass over a given number of degrees ($\Delta\theta$), say 5° C. or 10° C intervals.[25] The method, however, can not readily be made automatically recording for the variables θ and $dt/d\theta$ in terms of each other, and therefore requires the active presence of the observer. It has the same disadvantage as method II in that the precision of a difference in temperature (θ–θ' or $\Delta\theta$) can be made no greater than that of the temperature θ. The inverse rate method is perhaps best considered as one for interpreting and plotting the θ *vs* t data in such a way as to emphasize its irregularities and so the more readily permit the detection of any critical regions.

RAPID COOLING.

None of the experimental arrangements so far described is adapted for measuring the very rapid cooling, i. e., several hundred degrees in a few seconds, met with in quenching or chilling.

Le Chatelier,[26] in an investigation of the quenching of small samples of steel and the effect of various baths, made use of a galvanometer having a period of 0.2 second and a resistance of 7 ohms, whose deflections were recorded on a photographic plate moving vertically at a speed of 3 mm per second. A half second's pendulum vibrating across the path of the beam of light, from a Nernst glower as source, gave a measure of the time. He succeeded in recording satisfactorily temperature intervals of 700° C in 6 seconds, using as samples cylinders 18 mm on a side. It

[25] This method is well illustrated by F. Wüst, Metallurgie (German), **3**, p. 1; 1906.
[26] H. Le Chatelier, Rev. de Metallurgie, **1**, p. 473; 1904.

would be desirable to increase the precision and sensitiveness of this method, which might be done, as Le Chatelier himself suggests, by using an oscillograph arrangement, or a string galvanometer such as Einthoven's, in which the displacements of a silvered quartz fiber of high resistance in an intense magnetic field are measured photographically.

CHARACTERISTICS OF COOLING CURVES.

In conclusion, let us consider briefly the forms that the different cooling curves may take and their approximate interpretation, for three typical kinds of transformation:

(*a*) The substance remains at a constant temperature throughout the transformation.

(*b*) The substance cools at a reduced rate, which may or may not be constant over a portion of the transformation.

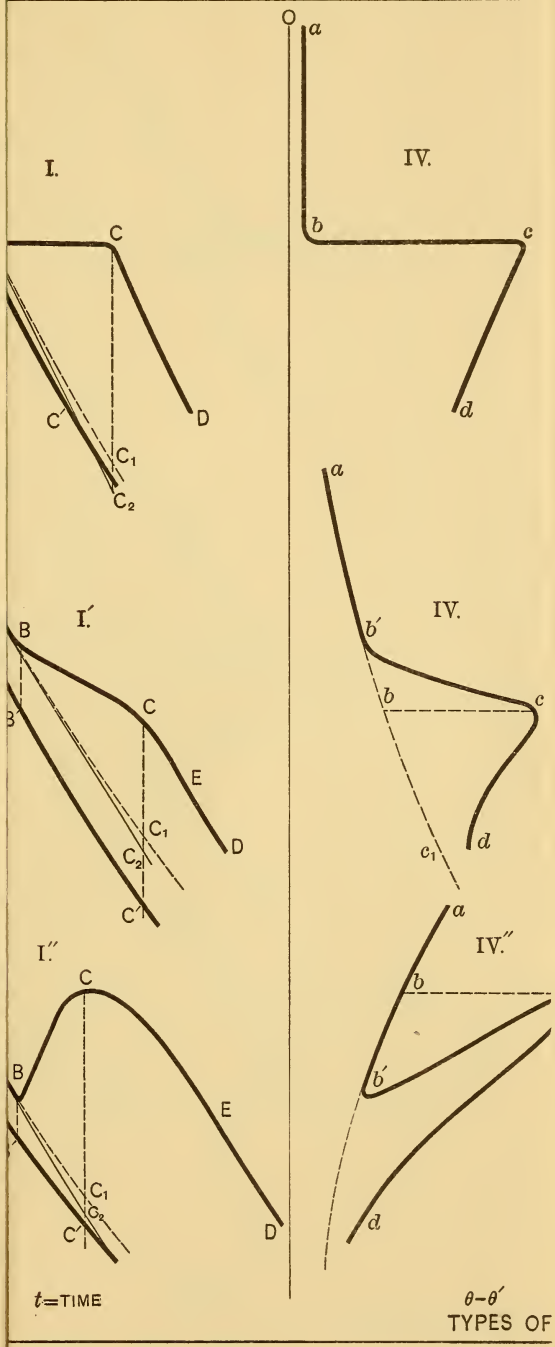
(*c*) The substance undergoes an increase in temperature during the first part of the transformation.

An approximation to the first case, that of a strictly isothermal transformation, is met with in the freezing of chemically pure substances of sufficient thermal conductivity which do not undercool appreciably; in the formation of eutectics; and occasionally in other transformations. The second case is perhaps the most common; and the third is represented by the phenomena of recalescence and of undercooling preceding crystallization.

In the case of an isothermal transformation (*a*) heat is generated at the same rate that it is lost by radiation, convection, and conduction, or, considering the phenomena as confined to the sample alone:

$$\frac{dQ}{dt} = Ms\ \frac{d\theta}{dt} \qquad (a)$$

where M is the mass, and s the specific heat of the body supposed constant during the transformation, $\frac{dQ}{dt}$ the rate of generation of heat, and $\frac{d\theta}{dt}$ the rate of cooling the body would have, when passing through the temperature of the transformation, if there were no transformation. The heat Q generated in such a transformation lasting a finite time Δt, is therefore:


I.
C
C′
C1
C2
D
I′.
B
B′
C
E
D
C1
C2
C′
I″.
C
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E
C1
C2
C′
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t=TIME
O
a
b
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d
IV.
a
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c1
IV.
a
b
b′
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IV″.
θ-θ′
TYPES OF

$$Q = Ms \frac{d\theta}{dt} \Delta t \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (\beta)$$

in which $\frac{d\theta}{dt} \Delta t$ is a measure of the fall of temperature, $\Delta\theta$ the substance would undergo if there were no evolution of heat during the time Δt, that is, during the transformation, whence:

$$Q = Ms.\ \Delta\theta \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (\gamma)$$

In the case of the transformation (*b*) we have

$$\frac{dQ}{dt} < Ms \frac{d\theta}{dt}$$

and for the transformation (*c*):

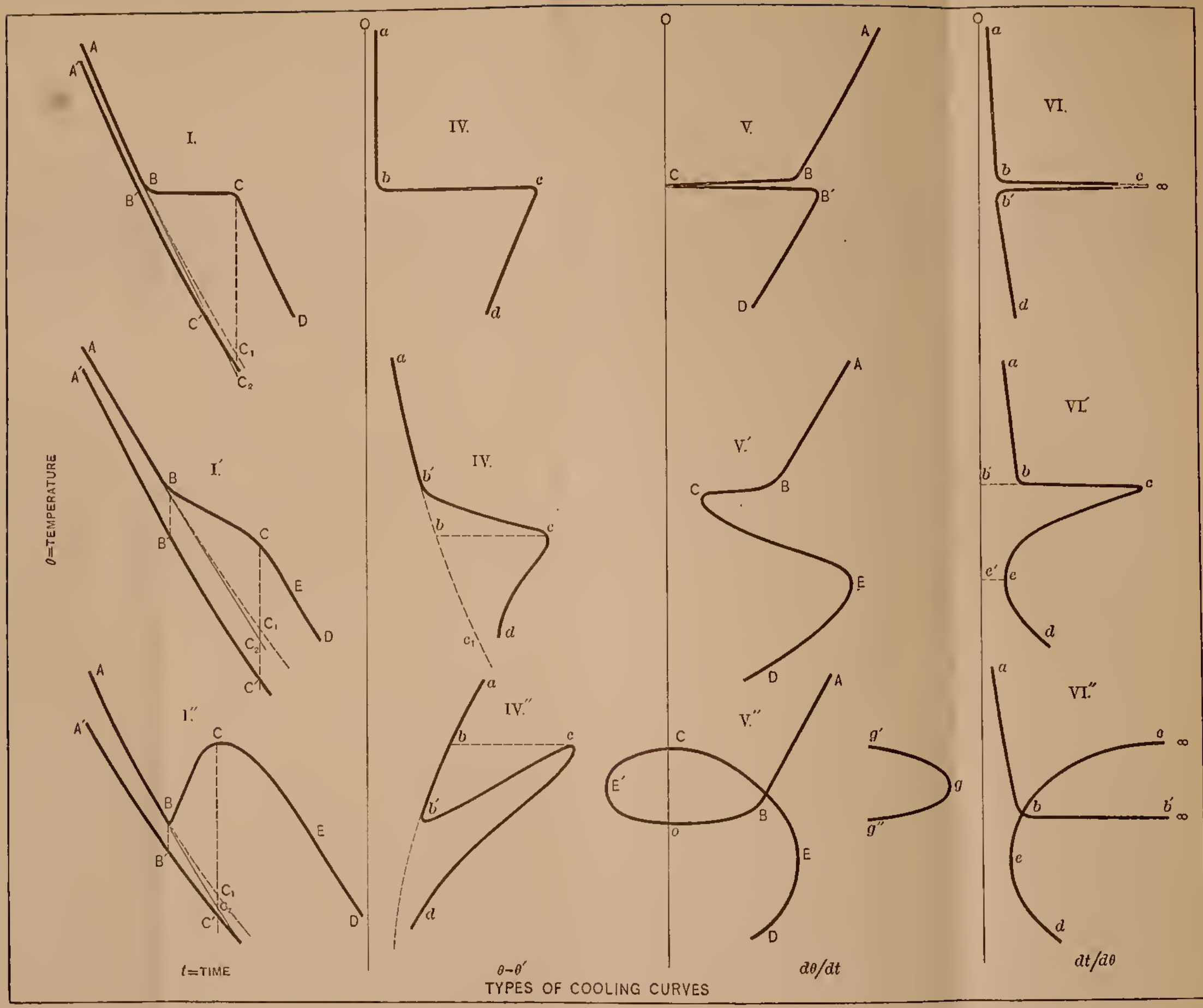
$$\frac{dQ}{dt} > Ms \frac{d\theta}{dt}$$

In Plate I are illustrated these three types of transformation as given by the following cooling curves:

I. θ *vs* t	Temperature-Time.
IV. θ *vs* $\theta - \theta'$	Differential.
V. θ *vs* $d\theta/dt$	Temperature-Rate.
VI. θ *vs* $dt/d\theta$	Inverse rate.

The first horizontal line of figures refers to case (*a*), the second line to (*b*), and the third line to (*c*). For all of the curves the ordinates are temperatures; and the corresponding parts of the several curves are indicated by the same letters. The vertical lines O, O, represent the zero of abscissæ for each group of curves.

In the case of the temperature-time curves, Figs. I, I′, I″, they are drawn for an accompanying neutral piece (p. 211), A′B′C′, as well as for the sample under study, ABCD. In I the sample and neutral are cooling at the same rate, while in I′ and I″ they are cooling at different rates. In each figure the point C_1 indicates the temperature that would have been reached by the sample if there had been no transformation. C_1 may be considered as practically coinciding with C_2, the temperature that would have been



TYPES OF COOLING CURVES

reached if the sample had continued to cool at the same rate as at B, the beginning of the transformation.

For each of these transformations (*a*), (*b*), and (*c*), as represented by the curves I, I′, I″, the heat evolved is approximately proportional to $\Delta\theta \doteq CC_1 \doteq CC_2$, or to the maximum difference in temperature produced by the phenomenon. It is to be noticed that in general the rate of cooling just to the right of C will be greater than that just to the left of B, on account of the presence of the furnace, for the furnace walls, to which the heat is being lost, have continued to cool during the time BC. Even if the furnace were at a constant temperature, the rates at B and C might still be different due to the difference in specific heats and in emissivities of the substance before and after the transformation. The end of a transformation is always marked by a point of inflexion as shown at E (Figs. I′, I″).

From the temperature-time curve, therefore, we may determine the temperatures of beginning and ending of a transformation, its duration, an approximate measure of the heat evolved by the transformation, as well as the rate of cooling and therefore of transformation, at any instant. The interpretation of the variations in these factors forms the basis of thermal analysis, which has already been so productive in the determination of the constitution of alloys and chemical compounds.[27]

Although the forms of the curves representing the various methods are those corresponding to what is actually obtained from a sample cooling inside a furnace, yet it should be noted that the equations representing the evolution of heat are written in a form that practically neglects the influence of the furnace.

A complete discussion of the cooling within a furnace of a substance possessing transformation points would be more complicated than contemplated by this paper; requiring a knowledge of the law of cooling of the furnace and that of the inter-

[27] The principles of thermal analysis as based on the θ *vs* t curve are quite fully described in the following papers by *Tammann:* Zs. Anorg. Chem., **37**, p. 303; 1903. **45**, p. 24; 1905. **47**, p. 289; 1905, a résumé of which is given by *Portevin* in Rev. de Metallurgie, **4**, p. 979; 1907. See also *Bancroft*, J. Phys. Chem., **6**, p. 178; 1902. *Shepherd*, ibid., **8**, p. 92; 1904, Iron and Steel Mag., **8**, p. 222; 1904, and *Bakhuis Roozeboom*, Die Heterogenen Gleichgewichte, 1901.

change of heat between the sample and the furnace, the latter depending on their relative heat capacities and conductivities, the emissivity of the sample, and the distribution of temperature within the furnace.

If small quantities of heat are involved in a transformation, the simplest assumptions that can be made are that at each instant the sample is losing heat to the furnace at a rate proportional to their difference in temperature, and that the parts of the furnace receiving this heat are all at the same temperature throughout at any instant. On this basis, the quantity of heat Q, lost by the sample during a transformation, as interpreted by the θ *vs* t curve, would be more nearly proportional to $\overline{CC^2_1}$ than to CC_1.

The practical conditions of cooling, however, are in general somewhere between the two extremes of the sample cooling independently of the furnace as required by our equations, and within the simplified furnace above described; so that CC_1 may be considered a minimum measure of the heat evolved, the actual measure of this quantity varying with every different experimental arrangement.

In what follows, the limitations just discussed, concerning the measurement of the heat evolved during a transformation, are assumed to apply to each of the types of cooling curve.

Figs. IV, IV′, and IV″ give the forms of the curves traced when the difference in temperature (θ–θ') between the sample and the neutral piece (p. 211) of approximately the same thermal capacity is plotted in terms of the temperature (θ) of the sample. In Fig. IV, the line *bc*, since it is the approximate equivalent of $CC_1 \doteq \Delta\theta$ of Fig. I, may be taken as a measure of the heat evolved during the transformation. If the cooling curves of the sample and of the neutral are not parallel, as shown in Figs. I′ and I″, it is necessary, in estimating the heat evolved from the difference curve *ab′cd* (Figs. IV′ and IV″) to take into account the variations in θ–θ' during the transformation. This change in θ–θ' is given by BB′—C_1C' (Figs. I′, I″). Furthermore, successive differential curves for the same sample are comparable only when the sample and neutral are cooled in the different

experiments so as to always maintain the same temperature-time relation over a given range. When this is the case, *bc* (IV′ and IV″) is still an approximate measure of the heat generated.

It can be shown that, except for horizontal tangents, the points of inflexion E of the θ *vs* t curves do not correspond to points of inflexion at the same temperatures on the differential curves, hence the end of a transformation can not be determined from the latter. If equal time intervals are marked on the differential curve, the rate of cooling or of transformation over an interval Δt may be obtained by finding the value of $\Delta\theta/\Delta t$.

Although, as we have seen (p. 210), the differential method may be made more sensitive and certain than the direct method, yet, from the above, it is evident that it furnishes a less complete basis for the interpretation of the physico-chemical phenomena involved in the indicated transformations.

Figs. V, V′, V″ represent the *temperature-rate* curves (θ *vs* $d\theta/dt$) and Figs. VI, VI′, VI″ the *inverse rate* curves (θ *vs* $dt/d\theta$). The two types may be considered as reciprocals of each other. Comparing them with the θ *vs* t curves (Figs. I, I′, II′) it is seen that a sharp break in the latter corresponds to a perpendicular to the temperature axis for both the former; and that for an isothermal transformation, $d\theta/dt$ becomes zero at C and $dt/d\theta$ infinite at *c*. When the θ *vs* t curve is convex to the θ axis, the $d\theta/dt$ curve is concave and the $dt/d\theta$ curve convex. Both curves give negative values (OE′C, Fig. V″, and *g′gg″* Fig. VI″) for a region of recalescence.

The end of a transformation, corresponding to a point of inflexion E on the θ *vs* t curve, is sharply indicated (E, *e*) on both these rate curves by the tangent becoming parallel to the θ axis and the curve having a maximum or minimum abscissa. For any region of cooling at a constant rate, the tangent remains parallel to the θ axis during this interval.

From neither of the rate curves can the relative amounts of heat evolved during a transformation be readily computed for the different kinds of transformation. The area of the inverse rate curve, however (Fig. VI′), taken between the limits *b′*, *e′* is proportional to Δt or to $Q/d\theta/dt$ (see equation β); that is, to the

quantity of heat generated divided by the rate of cooling.[28] If the rates of cooling at the beginning of two transformations are equal, then the areas, taken as above for the inverse rate curves (Fig. VI′), become an approximate measure of the heat generated. This condition, however, is rarely realized in practice. An examination of Fig. VI″ shows the practical impossibility of constructing any instrument other than one using an optical system, which would record the complete inverse rate curve.

We see, therefore, that both these rate curves mark the limits of a transformation more sharply than either the temperature-time or differential curves, and in general show greater changes in form for slight heat changes, but the rate curves do not in general give a simple measure of the heat evolved, nor is a neutral piece used to eliminate extraneous heat fluctuations.

A comparison of the properties of these various cooling curves indicates that the one from which the most comprehensive view of a transformation can be obtained is the simple temperature-time curve (I) when this method is made sufficiently sensitive; the one giving the least information is the temperature-rate curve (V); and those which cannot readily be recorded directly by any form of instrument yet devised are the inverse rate curve (VI) and the derived differential curve (IV*a*); while the one that can be made the most sensitive and certain is the differential curve (IV). The analytical discussion, therefore, leads to the same result as the examination of the experimental methods, namely, that for great range combined with greatest sensitiveness, the most certain and complete data may be obtained by combining the temperature-time observations with those obtained by the differential method.

WASHINGTON, August 3, 1908.

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[28] Area $b'bcee' = \int_{\theta_1}^{\theta_2} \frac{dt}{d\theta} d\theta = t_2 - t_1 = \Delta t$, or time occupied in falling a temperature $\Delta\theta$.

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